SCIENCE FOR GLASS PRODUCTION

PHYSICOCHEMICAL ASPECTS
OF MECHANOCHEMICAL ACTIVATION OF GLASS POWDERS

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A variant of the physicochemical interpretation involving the principles of thermodynamically irreversible processes is suggested to account for the effect of mechanicochemical activation of glass powders on milling cullet in highly intensive (impact-repulsion etc.) mills.

Mechanochemical activation of solid bodies is understood as a substantial increase in the chemical activity of powders resulting from the grinding of materials in highly intensive mills (planetary, impact-repulsion etc.). This effect is due not only to the increase in the specific surface area (S_{sp}) of the powders (i.e., the amount of non-compensated chemical bonds in the surface lattice sites of the material), but also to the perceptible deformation of the internal structure of the solid body particles.

The milling of window glass cullet in an impact-repulsion mill with the rotational speed of the beater equal to $9000 – 10,000$ min^{-1} and higher produces certain modifications in the structure of the glass powder particles and causes an increase in the crystallizing capacity of the glass when heated up to temperatures above t_g [1]. The present paper reflects an attempt at a theoretical interpretation of this phenomenon.

It is known that glass is the product of fast chilling of a highly viscous melt and its solidification without crystallization. Therefore, any glass contains excess internal energy ΔU and enthalpy ΔH, as compared to a crystalline material of the same chemical composition.

In fact, by equating the enthalpy value of the melt obtained by heating a crystalline material up to its complete melting

$$\Delta H_m = \Delta H_0^{cr} + \int_0^{t_m} C_p^{cr} dt + \Delta H_{melt}$$

to the enthalpy of the melt obtained by heating the preliminary obtained glass to complete melting

$$\Delta H_m = \Delta H_0^g + \int_0^{t_m} C_p^g dt,$$

we have

$$\Delta H_0^{cr} + \int_0^{t_m} C_p^{cr} dt + \Delta H_{melt} = \Delta H_0^g + \int_0^{t_m} C_p^g dt,$$

where H_0^{cr} and H_0^g is the enthalpy of glass and crystal which have the same composition, at $0°C$; C_p^{cr} and C_p^g is the heat capacity of the crystalline and vitreous materials within the temperature range from $0°C$ to t_m; t_m is the melting point of the crystalline material; ΔH_{melt} is its melting heat.

Hence

$$(\Delta H_0^g - \Delta H_0^{cr}) = \Delta H_0^g = \Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^g)dt.$$

This enthalpy excess H_0^g is almost equal (since $C_p^{cr} \approx C_p^g$) to the melting heat of the crystalline material accumulated by the system (the glass) and includes the energy consumed in breaking the bonds between the silicon-oxygen tetrahedra and other structural elements of the system in the course of the phase transformation (melting) and the modification in the $\equiv Si - O - Si \equiv$ bond angle in highly viscous melts.

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If the potential energy of all forces of chemical interaction in a crystalline material at room temperature is numerically equal to the crystal lattice energy (E_{lat} converted per 1 mole of material), obviously the potential energy of all chemical interaction forces in a glass of the same composition (let us denote it as the vitreous grid energy E_{gr}) per mole will be equal to

$$E_{gr} = E_{lat} - \left[\Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^{g})dt \right].$$

It is seen that $E_{gr} < E_{lat}$, which produces decreased hardness, mechanical strength, chemical stability, and the temperature of transition to the liquid state exhibited by glass, compared to the crystalline material of the same composition. All the above is true of crystals and glasses in the lump (single-phase) state.

In grinding (dispersion) of solid bodies, the specific surface area of the powder (S_{sp} per mole) increases with time. The destruction of the crystal lattice or the vitreous grid results in numerous ruptures of the internal (compensated) chemical bonds and their transition to the category of surface (non-compensated) bonds. The disperse system (the powder) on milling acquires a reserve of surface (non-compensated) energy which is equal to

$$E_S = \sigma_{surf} S_{sp},$$

where σ_{surf} is the specific surface energy of the milled material per surface area unit of the powder.

It follows from the energy conservation law that the remaining potential energy of interaction of the lattice points in the milled crystalline material particles is equal to (per 1 mole of material):

$$E_{mill}^{cr} = E_{lat} - E_S = E_{lat} - \sigma_{surf}^{cr} S_{sp}^{cr},$$

and for the milled vitreous material it is

$$E_{mill}^{cr} = E_{gr} - E_S = E_{lat}$$
$$- \left[\Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^{g})dt \right] - \sigma_{surf}^{g} S_{sp}^{g}.$$

The energy of the crystal lattice $A_p B_q$ with the prevailing covalent type of bonds (crystalline and vitreous silicates belong precisely to this type) can be estimated [2] using the following equation:

$$E_{lat} = \frac{1}{2} \varepsilon_{A-B}^{cr} N_A (n_A p + n_B q), \qquad (1)$$

where ε_{A-B}^{cr} is the energy of the single bond between the particles A in a crystalline material (for instance, Si and O): N_A is the Avogadro number; n_A and n_B are the coordination numbers of particles A and B in the lattice; p and q are the stoichiometric coefficients in the formula $A_p B_q$.

Equation (1) can be represented more generally as

$$E_{lat} = \frac{1}{2} N_A \sum \varepsilon_i^{cr} n_i p_i.$$

Then the vitreous grid energy will be equal to

$$E_{lat} = \frac{1}{2} \varepsilon_{A-B}^{cr} N_A (n_A p + n_B q)$$
$$- \left[\Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^{g})dt \right].$$

Hence

$$E_{mill}^{g} = \frac{1}{2} \varepsilon_{A-B}^{cr} N_A (n_A p + n_B q) -$$
$$- \left[\Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^{g})dt \right] - \sigma_{surf}^{g} S_{sp}^{g}.$$

In mechanochemical activation of cullet involving the extremely intensive methods, the mill rotor beaters apply numerous impacts on the glass particles which are constantly decreasing in size. The more powerful the impacts, the faster the material is destroyed. The velocity of crack propagation ($dx/d\tau$) inside a glass particle can be expressed by the formula [3]

$$\frac{dx}{d\tau} = \frac{\sigma_{max}^n}{\left[\dfrac{\partial}{\partial \tau} \left(\int_0^{\tau} \sigma_{max}^n \, d\tau \right) \right]},$$

where x is the crack depth (the coordinate calculated from the particle surface); τ is the current time; σ_{max} is the maximum shear (fracture, tensile) stress arising in the glass particles under the impact of the beater.

As the size of the pulverized glass particles decreases, the stresses which remained in the glass after annealing soon relax, but the impact waves pass at a high speed through these particles and lead to additional rupture of the $\equiv Si - O - SI \equiv$ bonds and the outcrop of dislocation steps on the glass surface. This additional store of non-compensated energy arising in the glass powder as a consequence of intense milling is the energy of mechanicochemical activation of material (ΔH_{mec} per 1 mole of material). According to estimates, it can comprise up to 5 – 7% milling energy transmitted to the solid body. Therefore, the potential interaction energy of the remaining internal sites of the vitreous grid in this case will be even lower:

$$E_{mill}^{g} = \frac{1}{2} \varepsilon_{A-B}^{cr} N_A (n_A p + n_B q)$$
$$- \left[\Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^{g})dt \right] - \sigma_{surf}^{g} S_{sp}^{g} - \Delta H_{mec}.$$

If we relate the "free" energy pumped to the glass $(\sigma_{surf}^{g} S_{sp}^{g} + \Delta H_{mec})$ to the initial (prior to milling) store of potential chemical interaction energy in the glass, we obtain the coefficient of material activation in the course of milling:

$$F = \frac{\sigma_{surf}^{g} S_{sp}^{g} + \Delta H_{mec}}{\frac{1}{2} \varepsilon_{A-B}^{cr} N_A (n_A p + n_B q) - \left[\Delta H_{melt} + \int_0^{t_m} (C_p^{cr} - C_p^{g}) dt \right]}. \quad (2)$$

It is obvious that the numerator in Eq. (2) reflect the thermodynamic instability of the "glass-air" disperse system (including the instability of the pulverized glass structure). The larger the numerator, the more active are the glass powders in the chemical, crystallizing, adsorption, and other aspects. In this case the total level of enthalpy of the pulverized glass, including the energy of the compensated and non-compensated bonds in the glass powder particles, increases as the energy "pumped in" from outside (from the crusher) increases. Figure 1. represents the dependence $H_g = f(t)$ for non-pulverized glass and for glass powders obtained under different milling conditions.

As the glass powders are heated, the oscillation amplitudes of the vitreous grid points increases, and the glass enthalpy becomes equal to

$$H_i^{g} = (H_0^{g})_i + \int_0^{t} C_{p_i}^{g} dt.$$

On further heating up to the crystallization temperature, diffusion mobility of the glass-modifying cations and the spinning and turning motions of the silicon-oxygen tetrahedrons are manifested; i.e., the thermodynamic instability of the glass powder structure is "supported" by the kinetic instability (thermal motion) of the glass grid points. Having attained the required energy level of activation of the crystallization process

$$E_A = \int_0^{t_{cryst}} C_p^{g} dt,$$

the glass spontaneously starts crystallizing and passes to the state of higher thermodynamic and kinetic stability. Obviously, since the level of E_A is equal, the glass with a higher
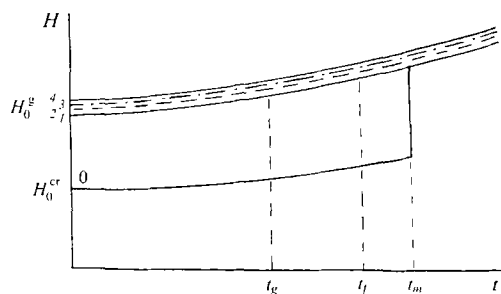

Fig. 1. Dependence $H = f(t)$ for: $0 - 1$) crystal; $1 - 1$) non-milled glass; $2 - 2$, $3 - 3$, and $4 - 4$) glass milled under different conditions where $f^2 < f^3 < f^4$ (f is the rotational speed of the mill rotor, min $^{-1}$).
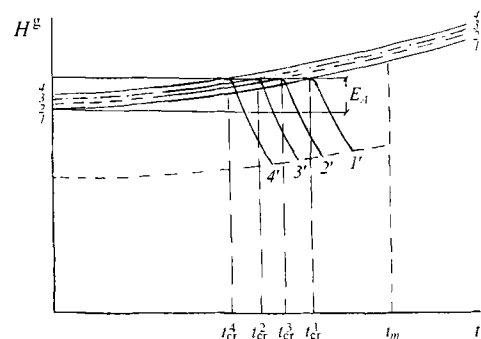

Fig. 2. Dependence $H = f(t)$ for glass crystallization processes: $1 - 1'$ initial glass; $2 - 2'$, $3 - 3'$, and $4 - 4'$) glass powders $(f^2 < f^3 < f^4)$.

initial level of (H_0^{g}) starts crystallizing sooner and $t_{cr}^{4} < t_{cr}^{3} < t_{cr}^{2}$ (Fig. 2)

This interpretation of the behavior of pulverized glass powders in heating well agrees with experimental data.

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